

# Treatment of Difficult Wastes with Molten Salt Oxidation

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# **Treatment of Difficult Wastes with Molten Salt Oxidation**

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## 1. Abstract

Molten salt oxidation (MSO) is a good alternative to incineration for the treatment of a variety of organic wastes such as explosives, low-level mixed waste streams, PCB contaminated oils, spent resins and carbon. Since mid- 1990s, the U.S. Army Defense Ammunition Center (DAC) and the Department of Energy (DOE) have jointly invested in MSO development at the Lawrence Livermore National Laboratory (LLNL). LLNL first demonstrated the MSO process for the effective destruction of explosives, explosives-contaminated materials, and other wastes on a 1.5-kg/hr bench-scale unit, and then in an integrated MSO facility capable of treating 8 kg/hr of low-level radioactive mixed wastes. Several MSO systems have been built with sizes up to 10 ft in height and 16" in diameter. LLNL in 2001 completed a MSO plant for DAC for the destruction of explosives-contaminated sludge and explosives-contaminated carbon. We will present in this paper our latest demonstration data and our operational experience with MSO.

## 2. Introduction

Molten salt oxidation (MSO) is a promising alternative to incineration for the treatment of a variety of organic wastes. It is a nonflame thermal treatment process and it completely destroys (oxidizes) the organic constituents of mixed wastes or hazardous wastes, including energetic materials, while retaining inorganic and radioactive constituents in the salt.

MSO technology is not new. Rockwell used the process more than 30 years ago for coal gasification, and they also demonstrated its effectiveness for destroying certain hazardous organics, such as PCBs and trichloroethylene. Extensive experience with laboratory-, bench-, and pilot-scale MSO units has been obtained at Rockwell, Oak Ridge National Laboratory, and Lawrence Livermore National Laboratory since the technology's introduction. Within the last 5 years, MSO also has been demonstrated as an effective method for destroying mixed waste oils and energetic materials.

Lawrence Livermore National Laboratory (LLNL) was tasked by the U.S. Department of Energy's Office of Environmental Management (DOE/EM) to demonstrate the MSO technology for the treatment of organic-based mixed wastes. Since early 1990, the LLNL's MSO/EM team has built several MSO units of different sizes, ranging from bench scale units, a 2-stage unit, to the 8" engineering-scale reactor unit (EDU). In 1997 the team built a facility in which an integrated pilot-scale MSO treatment system was demonstrated. The system consists of a MSO vessel with a dedicated off-gas treatment system, a salt recycle system, feed preparation equipment, and a ceramic final waste forms immobilization system. Over 30 different feed streams were demonstrated in the integrated MSO system from October 1997 to May 1999. These feed streams included surrogates and real waste streams, liquid and solid. Results of the demonstration have been documented and reported [1,2,3,4]. In a parallel development, LLNL has been tasked since 1992 by the U.S. DOE-DP, Air Force and Army Defense Ammunition Center (DAC) to demonstrate the MSO technology for the destruction of energetic materials. Several MSO systems were built and tested with a variety of energetic materials including ammonium picrate, HMX, RDX, TATB, TNT, Comp. B, LX-10, LX-16, and LX-17. In 2001, LLNL delivered a MSO plant to DAC for the treatment of explosives-contaminated charcoal. The system is operational with a process rate of 30 lbs slurry per hour [5].

### 3. Process Chemistry

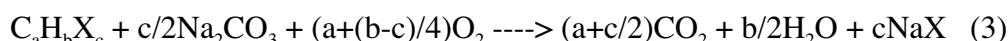
For the MSO process, organic wastes are injected with a stoichiometric excess of oxidant air under a pool of molten carbonate salts at temperatures between 700–950°C. Flameless oxidation takes place within the salt bath converting the organic components of the waste into CO<sub>2</sub>, N<sub>2</sub>, and water. The product off-gas leaving the processor is treated to remove any entrained salt particulate and essentially all water vapor before being discharged to the facility off-gas system. Halogens and heteroatoms such as sulfur are converted into acid gases, which are then “scrubbed” and trapped in the salt in forms such as NaCl and Na<sub>2</sub>SO<sub>4</sub>. Using sodium carbonate in the processor, this process occurs according to the reaction shown in Equations 1, 2, 3, and 4, where X represents generic halogens [6].



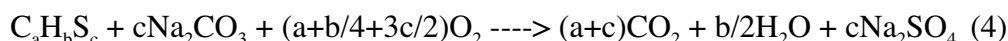
For nitrogen -bearing organic wastes,



For halogenated organic wastes,



For sulfur-containing organic wastes,



Other non-oxidizable -inorganic constituents, heavy metals, and radionuclides are held captive in the salt, either as metals or oxides, and are easily separated for disposal.

The salt remains in the bed catalyzing the destruction of waste until either the viscosity increases above acceptable levels or the carbonate salt is transformed into halide or heteroatom salts. Inorganic constituents captured in the bed eventually increase the bed viscosity above acceptable limits. These viscous salts are processed through the salt recycle system to remove the inorganic constituents and the salt is recycled to the bed.

Wastes that contain acid gas precursors such as chloride, sulfur and other heteroatoms eventually displace most of the carbonate in the salt to form the corresponding salts, for example sodium chloride. These salts are easily disposed of, especially in comparison to the similar volume of salts from an acid gas scrubber that must be disposed of when the wastes are processed in a conventional thermal treatment system.

Comprehensive testing and demonstration at Lawrence Livermore National Laboratory showed that process efficiencies as high as 99.9999% can be achieved at salt temperature above 900 °C.

### 4. System Description of MSO plant

The integrated MSO plant, shown in Figure 1, includes four systems: the MSO reactor system, the salt removal system, the pollution control system, and the feed preparation system.

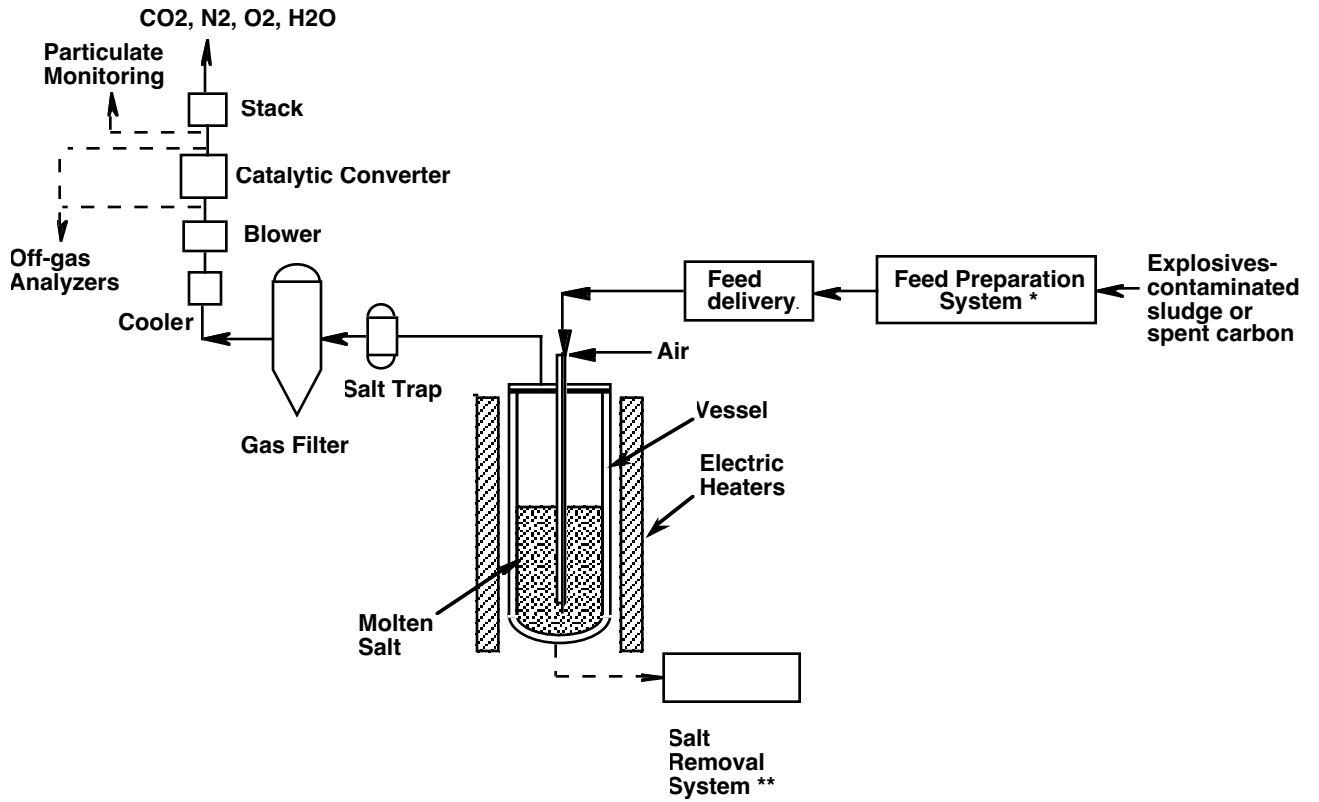
The MSO reactor system consists of a reactor vessel with heating, air delivery, and feed injector. The mixture of air and feed passes through the injector to the bottom of the reactor vessel. The salt removal system includes a receiving vessel, a secondary containment

drum, a vacuum ballast tank, and a vacuum system. There are several components in the pollution control system. These are: salt trap, hot gas filter, gas monitoring system, gas cooler, blower, catalytic converter, particulate monitoring device, and venting stack. The feed preparation system includes a feed separator, a size reduction unit (grinder), a product separator, a product storage drum with mixer.

The organic components of the feed react with oxygen in air to produce carbon dioxide, nitrogen and water. Quality of the off-gas leaving the reactor vessel is monitored continuously for CO, CO<sub>2</sub>, O<sub>2</sub>, THC (total hydrocarbon), SO<sub>x</sub>, and NO<sub>x</sub> by off-gas analyzers installed in the downstream of the gas filter during the MSO operation to evaluate the MSO process efficiency. Discrete off-gas samples may be collected in the sample collection system for analysis of volatile and nonvolatile organic compounds. The catalytic converter is a major component in the pollution control system. It is designed to remove 90% of NO<sub>x</sub>, 95% and further oxidize 95% of CO and THC in the off-gas.

Most inorganic components of the feed are captured in the molten salt bed. Halogenated hydrocarbons in the feed generate acid gases such as hydrogen chloride which is then scrubbed by the alkaline carbonates and converted to chloride and stayed in the salt bed. Long term operation of the MSO reactor system may lead to the depletion of the carbonates and contamination of the salt bath with inorganic constituents from the feed. As a result, the salt will have to be replaced. The salt can be removed by the salt removal system.

Figure 1: MSO Plant Process Flow Diagram



\* Feed preparation system includes a feed separator, a size reduction unit, a product separator, a product tank with mixer, and a pump

\*\* Salt removal system consists of two salt tanks, a vacuum ballast tank, and a vacuum pump.

## 5. Demonstration Results

Many waste streams were treated in several LLNL-built MSO plants since mid-1990s and some of results were documented and reported. In this paper, we will report results from the MSO testing with several solids and PCB-contaminated liquids.

### 5.1. Results of Testing with Solids

Surrogate materials including ABS plastic pellets, shredded booties and gloves, ion exchange resin (Amberlite), and activated carbon were demonstrated. For each run in the test series, some gas samples were also collected and sent to a laboratory for analysis. Table 1 shows the run conditions for the test series. The solid feeds were fed to the MSO vessel with a vibratory feeder and an eductor and carried into the molten salt bed by the compressed air. A large excess of process air was provided for these runs to overcome the feedrate fluctuation from the vibratory feeder. A larger size of ABS pellet (3.0 to 5.5 mm) was also tested but the off-gas quality was not good, probably because this increased the residence time of the pellet in the molten salt bed to complete the oxidation process. It was found that solid particles less than 3.0 mm can be effectively treated by the MSO process if sufficient excess air is provided. The off-gas composition for these runs is shown in Table 2.

Table 1: Run Conditions

No.	Feeds	Run Conditions
1	ABS pellets (2.5 mm)	950°C, 1.45 kg/hr, 58% excess air
2	Shredded booties	950°C, 1.88 kg/hr, 65% excess air
3	Ion exchange resin (Amberlite)	950°C, 3.0 kg/hr, 40% excess air

Table 2: Off-gas Composition for the Solid Feeds

Off-gas Species	Run Numbers		
	1	2	3
CO <sub>2</sub> , %	9.4	8.4	12.9
O <sub>2</sub> , %	9.3	11.2	6.2
CO, ppm	18.6	154	17
NO <sub>x</sub> , ppm	306	6.9	150
SO <sub>x</sub>	0.0	0.0	0.0
THC	2.0	1.0	0.4

The values in the Table 2 were taken from the off-gas analyzer readings at steady feed rate, they varied when the feed rate fluctuated and may reach as high as 80 ppm for THC, and 400 ppm for NO<sub>x</sub> and CO, respectively. Although it is desirable to have a solid feeder



which can deliver a constant feed to the MSO vessel, the feed rate variation can be overcome with a large excess of process air. The higher levels of  $\text{NO}_x$ ,  $\text{CO}$ , and ThC in the off-gas system can be further reduced in the catalytic converter before venting to the facility stack.

## 5.2 Test Results with PCB-contaminated Wastes

PCB-contaminated wastes are difficult to treat by incineration due to the formation of dioxins and furans, cancer-causing agents, at the incineration temperature. To demonstrate that MSO is an efficient alternative to treat these wastes, 5 gallons of a PCB-contaminated waste specimen was fed into the process vessel as part of the treatability study. The main objective of the experiments was to show that dioxin and furan emissions from the system were below the proposed regulatory limit of  $100 \text{ pg/m}^3$  gas as 2,3,7,8-tetrachlorodibenzo-para-dioxin equivalents or toxic equivalence quotient.

Dioxins and furans are a group of related compounds which are suspected of having harmful effects in humans. Laboratory tests have shown that 2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-para-dioxin), one of most toxic compounds in the group, can cause cancer and toxic effects in laboratory animals. Hence their emissions from a thermal treatment process are subjected to strict regulations. EPA proposed that the regulatory limit for dioxin and furan emissions from hazardous waste treatment systems be  $100 \text{ pg/m}^3$  toxic equivalence quotient (TEQ). The toxic equivalence factor (TEF) of a particular dioxin or furan is defined as the ratio of its toxicity to the toxicity of 2,3,7,8-TCDD, which has a TEF of 1.

The PCB-contaminated waste was delivered to the MSO facility from the Waste Management Division of LLNL in a five-gallon container. The waste was sampled and sent for analysis. Table 3 shows the composition of the waste. Toluene was used as a diluent to reduce the viscosity of the waste for the ease of feed delivery. The waste, containing mostly hydraulic oil with over 1000 ppm PCB and traces of metals and radionuclides was fed into the MSO system at 1.1 kg/hr along with 30% excess air for 13 hours. The molten salt bed, containing 160 kg sodium carbonate, was controlled at  $950^\circ\text{C}$  during the course of the demonstration. The GSS (gas/solid separation) filter was backflushed with compressed air periodically to prevent excessive buildup of salt cake in the filter element.  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{SO}_x$  in the off-gas were continuously monitored with off-gas analyzers. Sampling was conducted from the sampling ports located on the inlet and outlet of the GSS filter and from the catalytic converter outlet. The sampling ports were located to meet the 8 duct diameter downstream and 2 duct diameter upstream from any points of flow disturbance criteria. Best Environmental, Inc. handled the off-gas sampling operation during the demonstration. All the collected samples were sent to EPA-certified laboratories for analysis.

Table 3

	Oil/PCB
chloroform (g/L)	ND
1,1-dichloroethane (g/L)	ND
1,2-dichloroethane (g/L)	ND
1,1-dichloroethene (g/L)	ND
dichloromethane (g/L)	ND
tetrachloroethane (g/L)	ND
toluene (g/L)	2.9
dichloroethene	1.7
trichloroethene (g/L)	ND
1,1,2-trichloro, 1,2,2 trifluoroethane (g/l)	14
methylchloroform (g/L)	11
Sb (mg/L)	ND
Ba (mg/L)	2.6
Be (mg/L)	ND
Cd (mg/L)	ND
Cr (mg/L)	0.38
Co (mg/L)	ND
Cu (mg/L)	1.7
Pb (mg/L)	7.4
Mo (mg/L)	0.3
Ni (mg/L)	ND
K (mg/L)	ND
Ag (mg/L)	0.07
U (mg/L)	11.5
V (mg/L)	ND
Zn (mg/L)	2.3
Hg (mg/L)	0.35
Hydraulic oil, (g/L)	862.5
PCB, mg/L	1567
Gross Alpha (nCi/L)	7.8
Gross Beta (nCi/L)	0.85
(Tritium (nCi/L))	38

The off-gas quality, as shown in Table 4 was very good with less than 50 ppm NO<sub>x</sub>, less than 20 ppm CO, and nondetectable THC in the off-gas. Table 5 shows that feed rates and emission rates of POHCs, total dioxins and furans, volatile organics, total semivolatile organics, particulate, gross alpha, gross beta, and HCl. The particulate emission rate was 0.0000034 lbs/hr at average off-gas flow rate of 13.8 dscfm or only 0.0000016 g/ft<sup>3</sup>. The destruction efficiencies of the POHCs were greater than 99.99%.

Table 6 shows the results of dioxin and furan emissions. Gas samples were taken from the GSS filter inlet and the outlet of the catalytic converter. The table shows the emission rate and concentration of each individual dioxin and furan and its TEF and TEQ. TEQ is the concentration of each individual dioxin and furan multiplied by its TEF. As shown in the table, the total dioxin and furan emissions from the GSS filter inlet and the catalytic converter outlet were 38.743 pg/m<sup>3</sup> TEQ and 9.338 pg/m<sup>3</sup> TEQ, respectively. These emissions are well below the EPA proposed regulatory limit of 100 pg/m<sup>3</sup>.

Table 4: Off-gas Composition

<u>Off-gas Species</u>	
CO <sub>2</sub> , %	7.3
O <sub>2</sub> , %	10.1
CO, ppm	15.6
NO <sub>x</sub> , ppm	27.3
SO <sub>x</sub>	0.0
THC	0.0

\*The numbers were taken directly from the readings of the off-gas analyzers.

Table 5: Feed Rates, Emission Rates, and DREs

<u>Test Parameter</u>	<u>Feed Rate to the MSO Vessel</u>	<u>Emission Rate</u>	<u>DRE %</u>
MCM	0.168 g/min	<0.291 $\mu$ g/min	>99.999827
1,1-dichloroethene	0.025 g/min	1.073 $\mu$ g/min	99.99571
Tetrachloroethene	N.A.	<0.166 $\mu$ g/min	N.A.
Trichloroethene	N.A.	<0.187 $\mu$ g/min	N.A.
Trichloro-trifluoroethane	0.213 g/min	<4.151 $\mu$ g/min	>99.99805
Toluene	2.78 g/min	1.069 $\mu$ g/min	99.999962
Total PCB	0.0233 g/min	<0.0414 $\mu$ g/min	>99.99982
Hydraulic oil	14.98 g/min	N.A.	N.A.
Total Dioxin/Furan	None	108.86 pg/min	N.A.
VOST Volatiles	N.A.	<17.82 $\mu$ g/min	N.A.
Semi-volatiles	N.A.	<95.854 $\mu$ g/min	N.A.
Particulate	N.A.	0.000034 lbs/hr	N.A.
Gross Alpha	8,140 pCi/hr	15.53 pCi/hr	N.A.
Gross Beta	890 pCi/hr	0.961 pCi/hr	N.A.
Tritium	39,700 pCi/hr	3,564,582 pCi/hr	N.A.
HCl	N.A.	<0.0015 g/hr	N.A.

Table 6: Results for Dioxins and Furan Emissions

Species	TEF	@ GSS Filter	TEQ	@ Catalytic Converter	TEQ
		Thlet, pg/m3	pg/m3	Outlet, pg/m3	pg/m3
2,3,7,8-TCDD	1	22.301	22.301	7.506	7.506
TCDF	0.1	78.954	7.895	3.503	0.350
PeCDF	0.05	50.310	2.516	5.505	0.275
HxCDF	0.1	12.521	1.252	1.426	0.143
HpCDF	0.01	4.204	0.042	1.051	0.011
OCDF	0.001	2.742	0.003	1.776	0.002
PeCDD	0.5	8.527	4.264	1.877	0.939
HxCDD	0.1	3.593	0.359	1.001	0.100
HpCDD	0.01	4.684	0.047	1.101	0.011
OCDD	0.001	64.379	0.064	2.352	0.002
		Total TEQ	38.743		9.338

## 7. Conclusions

The MSO technology is effective in treating some difficult waste streams such as low-level mixed wastes, chlorinated solvents, PCB contaminated oils, and energetic materials. It operates at lower temperatures than incineration and generation of secondary wastes such as spent salt appears to be manageable. It offers a valuable alternative to incineration. The further implementation of MSO technology at the industrial scale with real waste streams is very important to bring the technology to a wider acceptance by the public and the waste management industry

## ACKNOWLEDGEMENTS

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